

Effect of Grain Size on the Corrosion Behavior of TiAlBN Nanocomposite Coating

Zulkifli M. Rosli^{1,a}, Wai Loon Kwan^{*1,b}, Jariah M. Juoi^{1,c}, Nafarizal Nayan^{2,d}, Zainab Mahamud^{1,e} and Yusliza Yusuf^{1,f}

¹Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

²Faculty of Electrical & Electronic Engineering, Universiti Tun Hussein Onn Malaysia Johor, 86400 Parit Raja, Batu Pahat Johor, Malaysia

^azmr@utem.edu.my;

^{*b}kwailoon86@gmail.com; ^cjariah@utem.edu.my; ^dnafa@uthm.edu.my; ^ezainab.mahamud86@gmail.com; ^fyusliza@utem.edu.my

Abstract

TiAlBN nanocomposite coating have been deposited by varying nitrogen-to-total gas flow rate ratio (R_N) of 5, 15, 20, 25%, and varying substrate temperature of 100, 200, 300, and 400 °C. The coating was deposited on AISI 316 substrates using radio frequency (RF) magnetron sputtering with single Ti-Al-BN hot-pressed target. The crystallographic phase, structural, and grain size was evaluated using glancing angle X-ray diffraction analysis (GAXRD). The corrosion behavior of the coating was determined using potentiodynamic polarization test. The grains size of the deposited coating (calculated using Scherrer's formula) were found to be in the range of 3.5 to 5.7 nm. It was also found that the grain size affects the corrosion behavior of the coating in which larger grain size decreases the corrosion resistance of the deposited TiAlBN nanocomposite coating. In addition, it was observed that the corrosion resistance of the coating is lower than the substrate material. Nevertheless, the coating was able to protect the surface of the uncoated AISI 316 substrate from pitting corrosion. Moreover, the coating exhibited a corrosion resistance comparable with other high corrosion resistance coatings such as (Ti,Al)N, and TiAlSiN.

Keywords

TiAlBN; Nanocomposite; GAXRD; Polarization; Grain Size; Corrosion Potential; Corrosion Current Density

Introduction

Tribological coatings are commonly used for cutting tools, forming tools, and machine parts including bearing, brakes, bolted joints, seal, and valves. These are all examples of application in which wear and friction are frequently occurred. Usually, tribological coatings are produced with high hardness, chemically inert, and possess excellent wear resistance. Thus,

when applied on tools and parts, the surfaces beneath the coating are well protected from wear, friction, and chemical attacks, hence increases their lifespan. Some examples of the tribological coatings are titanium nitride (TiN), titanium carbide (TiC), and diamond-like carbon (DLC). Among them, the TiN coating is the most explored hard coating due to its excellent tribological properties (Holmberg and Matthews 1998). However, studies had found that TiN suffers from low oxidation resistance which is up to 500 °C (Desmaison et al. 1979). This is a disadvantage when cutting tool tips may be heated up to temperature above 500 °C in some machining operation (Zukerman et al. 2007).

In order to improve the oxidation resistance as well as other properties (e.g. mechanical and tribological) of TiN, incorporation of one or more atoms such as B, Al, Si, and Cr into the TiN binary system has been actively explored. Among them, TiAlBN coating has been attracting more attention due to its superior properties than most hard coatings such as TiAlN, and TiBN. TiAlBN coatings present a nanocomposite feature where nanocrystalline (nc) (Ti,Al)N phase are embedded in amorphous (a) BN and/or a-TiB₂ phase (Hernandez et al. 2004, Rebholz et al. 2007, Baker et al. 2010). This feature grants the TiAlBN nanocomposite coatings with excellent hardness, wear resistance, thermal stability, and long-term stability (Hernandez et al. 2004, Rebholz et al. 2007, Rebholz et al. 1999, Baker et al. 2002). However, the corrosion behavior of the coating has received limited attention. A study of corrosion behavior is relatively important, especially when it is applied on materials such as steel which are frequently subjected to corrosive environment. One of the factor influence the corrosion behavior of a

nanocomposite is believed to be related to grain size (Barshilia et al. 2006).

A recent review by Ralston and Birbilis (2010), several engineering materials could experience an increase or decrease in corrosion resistance with grain refinement depending upon the ability of the environment to passivate. In a passive environment, grain refinement increases corrosion resistance and vice versa in active environment. In terms of thin coating, similar deduction was also observed. In NiTiAl coatings which are able to form passive layer of TiO_2 and Al_2O_3 , it was found that smaller grain size in the NiTiAl coating showed enhanced corrosion resistance as compared to a coarse grain coating (Liu and Duh 2008). The tests were done in a passive environment. The enhancement was attributed to the higher grain boundary density in fine structure which encourages the formation of noble and protective passive film. In addition, it was believed that the reduction of the grain size is also related to the corrosion resistance enhancement of a nanocomposite coating (Barshilia et al. 2006). It was also found that nanocomposite coating such as $\text{TiAlN}/\text{Si}_3\text{N}_4$ showed an improvement in corrosion resistance as the grain size of the coating reduces. The reduced grain size was due to the increase of amorphous Si_3N_4 .

Meanwhile, report on the corrosion behavior of TiAlBN nanocomposite coating is very limited reflecting on the less studies of this behavior. Therefore, more work is required to determine the performance of this coating. In present study, the effect of grain size on the corrosion behavior of the TiAlBN nanocomposite coating is reported. The corrosion behavior of the TiAlBN nanocomposite coatings is analyzed via an electrochemical test.

Experimental Setup

Substrate Materials

The principle substrate material used in this study is AISI 316 stainless steel disc with dimension of $\text{Ø}15 \text{ mm} \times 3 \text{ mm}$. Prior to the cleaning process, the substrates surfaces were grinded and polished using $3 \mu\text{m}$ alumina paste to obtain a mirror surface. Other than AISI 316, silicate glass was also used as substrate specifically for GAXRD analysis. The AISI 316 and glass substrate were ultrasonically cleaned to remove organic contaminations on the surfaces. Ultrasonic cleaning in acetone bath was first carried out for 10 minutes, followed by ethanol bath for another 10

minutes. After that, the substrates were rinsed with distilled water and allowed to dry to avoid formation of residue from the ethanol bath.

TiAlBN Nanocomposite Coating Deposition

The TiAlBN nanocomposite coatings were deposited using PSP5004 SNTEK radio frequency (RF) magnetron sputtering. The target material for the deposition process with the dimension of $\text{Ø}76.2 \text{ mm} \times 6 \text{ mm}$ was made of a hot-pressed mixture of titanium, aluminium, and boron nitride powders with 99.9% purity. The powders mixture consist of 70 wt.% Ti, 15 wt.% Al, and 15 wt.% BN. Utilizing this composition, low amount of aluminium in the deposited coating can be obtained to produce a hard nc-(Ti,Al)N/a-BN/a- TiB_2 nanocomposite (Hernandez et al. 2004, Shtansky et al. 2001). Prior to deposition, the target was sputter cleaned in argon environment at 100 W power, and 20 mtorr working pressure for 20 minutes. The fixed parameters used for the deposition process are shown in Table 1. The TiAlBN nanocomposite coatings were deposited at various nitrogen-to-total gas flow ratio (R_N) of 5, 15, 20, and 25%, and various substrate temperature of 100, 200, 300, and 400 °C. The deposited coating thickness determined using Alpha-Step IQ surface profiler was in range of 0.65-0.99 μm .

TABLE 1 FIXED PARAMETERS USED FOR DEPOSITION OF TIALBN NANOCOMPOSITE COATING

Parameter	Value
Power Mode	RF
Target Power (W)	400
Power Density (W/cm ²)	8.77
Bias Voltage (-V)	60
Base Pressure (torr)	<5×10 ⁻⁶
Target to Substrate distance (cm)	14
Time (min)	90

Crystallographic Phase, Structural and Grain Size Evaluation

The crystallographic phase, structure, and grain size were determined using PANalitycal's glancing angle X-ray diffraction (GAXRD) at an angle of 2°. The X-ray was generated from a $\text{CuK}\alpha$ target operating at 40 mA and 40 kV. The divergence slit size used was 0.8709°. A continuous 2θ scan from 0 – 90° was conducted with step size of 0.01° and speed of 0.02° s⁻¹. The crystallite phase and structure were evaluated based on the obtained GAXRD spectra. In addition, the full-width

at half-maximum (FWHM) of the Bragg peaks are used to calculate the grain size according to Scherrer formula:

$$D_p = K \lambda / (B \cos \theta)$$

where λ is the X-ray wavelength, B is the FWHM of the Bragg peak in radian, θ is the Bragg's angle in radian, and K is the dimensionless constant dependent on crystallite shape. For a cubic shape grain of TiN (determined from the GAXRD spectrum), K is denoted as 0.94 (Niederberger and Pinna 2009).

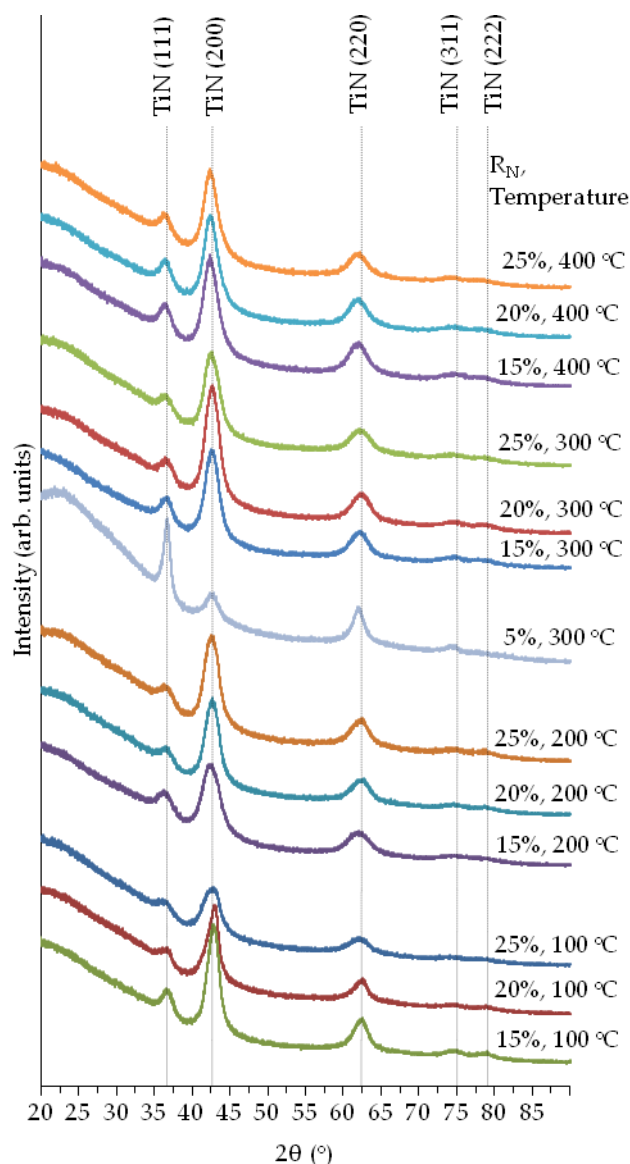


FIG. 1 GAXRD SPECTRA OF THE DEPOSITED TiAlBN NANOCOMPOSITE COATINGS AT VARIOUS R_N AND SUBSTRATE TEMPERATURE (INCIDENT ANGLE OF 2°)

Corrosion Behavior

The corrosion behavior of the coating was assessed by means of potentiodynamic polarization technique. The test was conducted according to ASTM G3-89

standard. The experimental setup used is as shown in Table 2. The counter electrode used was graphite rod, while the reference electrode used was Ag-AgCl in a Luggin capillary. 3.5 wt% salt solution that resemble artificial seawater was prepared as electrolyte.

TABLE 2 FIXED PARAMETERS FOR POTENTIODYNAMIC POLARIZATION DATA ACQUISITION

Experimental Setup	Value
Initial E	-0.6 V
Final E	0.9 V
Scan Rate	1 mV/s
Sample Period	1 s
Sample Area	1.7671 cm ²
Density	7.99 g/cm ³
Equivalent Weight	25.5

TABLE 3 GRAIN SIZE OF THE DEPOSITED TiAlBN NANOCOMPOSITE COATINGS CALCULATED USING SCHERRER FORMULA

Substrate Temperature (°C)	Grain Size (nm)			
	5% R_N	15% R_N	20% R_N	25% R_N
100	-	5.5	4.8	3.8
200	-	3.5	4.1	4.6
300	5.7	4.6	4.9	4.2
400	-	4.1	4.3	4.4

Results

Crystallographic Structure and Grain Size

The GAXRD patterns of the deposited TiAlBN nanocomposite coatings at various nitrogen-to-total gas flow rate ratio (R_N) and substrate temperature are shown in Fig.1. All of the deposited coatings showed diffraction peaks corresponding to TiN phase at plane (111), (200), and (220). However, the presence of TiB_2 and BN phases were not detected. These phases were confirmed to exist as an amorphous through XPS analysis as presented in the paper by Rosli *et al.* (2013). In addition, the Al atoms in the coating is known to incorporate into the TiN lattice to form the (Ti,Al)N phase (Rosli *et al.* 2013). From the GAXRD patterns, it was found that the intensity of the peak at plane (111) and plane (200) were affected by the R_N used. For lower R_N (5%), highest peak was belongs to plane (111). However, at R_N of 15% and above, the highest peak had switched to plane (200). In addition, it was observed that there was no broadening of the diffraction peaks for all the deposited coatings despite

varying the R_N and substrate temperatures. The grain size of the crystallite phase calculated using Scherrer formula for all the deposited TiAlBN nanocomposite coating were in the range of 3.5 to 5.7 nm as shown in Table 3.

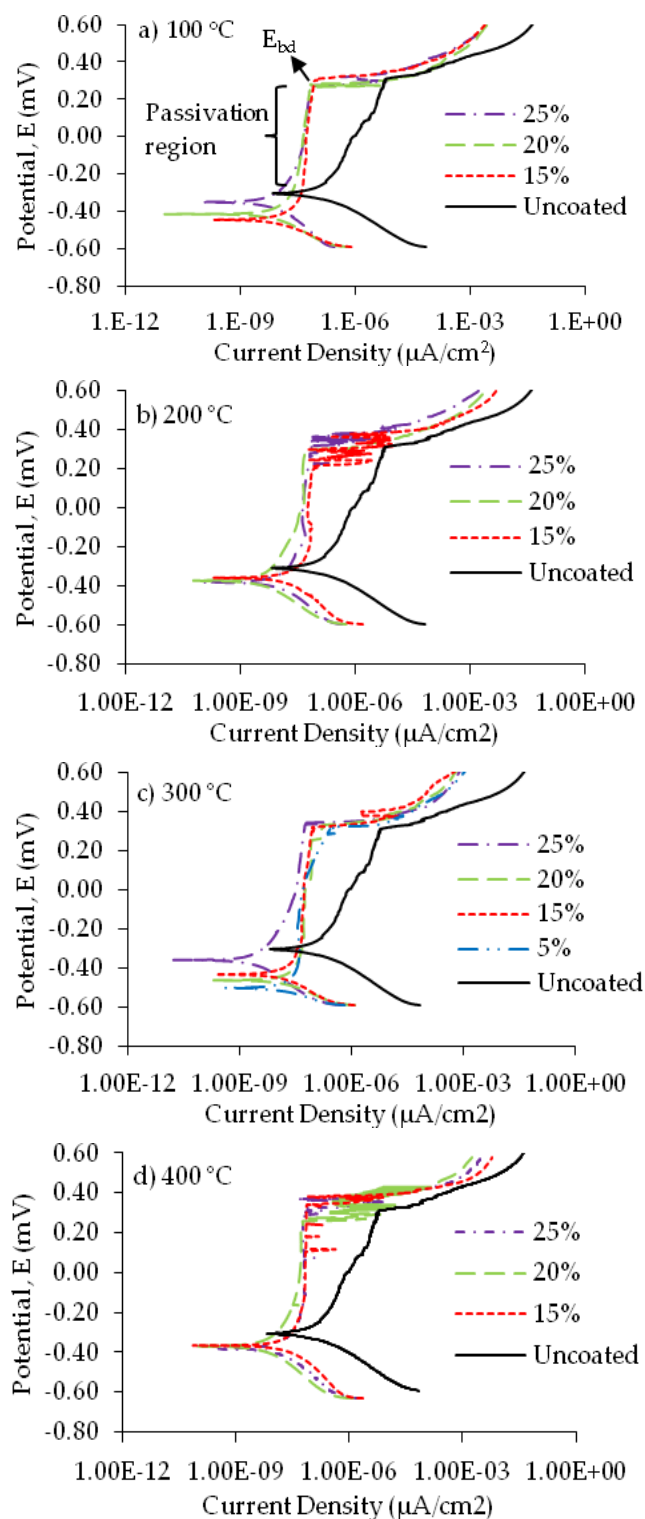


FIG. 2 POTENTIODYNAMIC POLARIZATION CURVE OF TIALBN NANOCOMPOSITE COATINGS DEPOSITED BY VARYING R_N AT SUBSTRATE TEMPERATURE OF A) 100 °C B) 200 °C, C) 300 °C, AND D) 400 °C

Corrosion Behavior

The potentiodynamic polarization curves of the deposited TiAlBN nanocomposite coatings by varying R_N and varying substrate temperature are shown in Fig. 2. Meanwhile, the corrosion current density of TiAlBN nanocomposite coatings deposited at various R_N and temperature are illustrated at Fig. 3. From Fig. 2, all TiAlBN coated samples showed a much better corrosion behavior than uncoated steel, in terms of current density, i_{corr} value and its passivity region. Upon anodic polarization, significant decrease in i_{corr} can be observed for all the TiAlBN coated samples. The i_{corr} of the TiAlBN coated samples were in the range of 9.9 - 66.8 nA/cm^2 (Fig. 3) as compared to 126.2 nA/cm^2 exhibited by the uncoated sample. Moreover, the passivity regions of the TiAlBN coated samples were much narrower than the uncoated sample. The low i_{corr} and narrower passivity region indicates that the TiAlBN coated sample exhibit a much lower corrosion rate as compared to the uncoated sample. Other than that, it can be clearly seen that the i_{corr} were not affected either by the R_N or the substrate temperature.

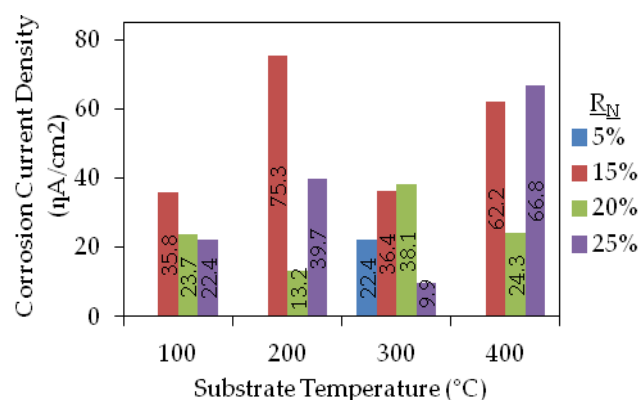


FIG. 3 CORROSION CURRENT DENSITY, i_{corr} OF TIALBN NANOCOMPOSITE COATINGS DEPOSITED BY VARYING R_N AND SUBSTRATE TEMPERATURE

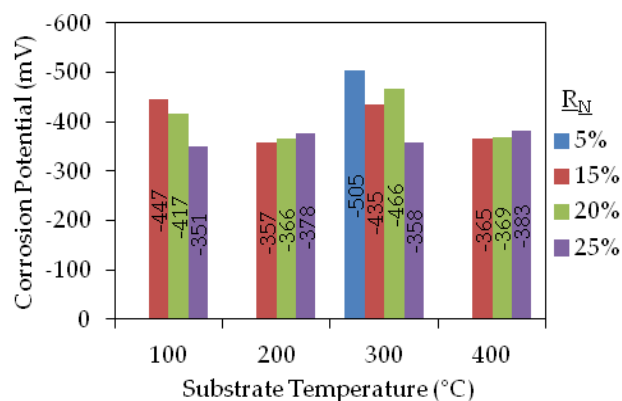


FIG. 4 CORROSION POTENTIAL, E_{corr} OF TIALBN NANOCOMPOSITE COATINGS DEPOSITED AT VARYING R_N AND SUBSTRATE TEMPERATURE

Fig. 4 shows the corrosion potential, E_{corr} , of TiAlBN nanocomposite coatings deposited by varying R_N and temperature. The E_{corr} of the TiAlBN coated samples were in the range of -351 to -505 mV as compared to -308 mV of the uncoated sample. The lower E_{corr} signifies that the corrosion of the TiAlBN coated samples initiate more quickly than the uncoated sample. Other than that, it can be observed that the E_{corr} are not affected by either R_N or substrate temperature.

Meanwhile, it can be noted that the breakdown potential (E_{bd}) that indicates the start of pitting corrosion is the same for all samples as observed in Fig. 2. The fact that the TiAlBN coated samples showed the same E_{bd} as the uncoated sample is probably due to surface defects such as flaking presented in the coating which cause the substrate surface of the AISI 316 to be exposed to pitting corrosion (Rudenja et al. 1999).

Discussion

In this study it was found that the TiAlBN nanocomposite coatings exhibit a good corrosion resistance indicated from the low corrosion rate of the coated sample (based on low i_{corr} value). The low corrosion rate is attributed to the presence of titanium and aluminum atom within the TiAlBN nanocomposite coating itself. These atoms are known for being able to form a high corrosion resistant passive layer of TiO_2 and Al_2O_3 (Liu and Duh 2008). In addition, the corrosion resistance of the TiAlBN nanocomposite coating is also comparable with other high corrosion resistance nanocomposite coating such as TiAlN (Yoo et al. 2008), and TiAlSiN (Barshilia et al. 2010) based on the data acquired such as the corrosion potential and corrosion current density as shown in Table 4.

TABLE 4 CORROSION POTENTIAL AND CORROSION CURRENT DENSITY COMPARISON FOR TIALBN, TIALN, AND TIALSiN COATING

Coating	Corrosion Potential, E_{corr} (mV)	Corrosion Current Density, i_{corr} ($\mu\text{A}/\text{cm}^2$)	Reference
TiAlBN	-358	0.0099	This work
TiAlN	-439	2.23	Yoo <i>et al.</i> 2008
TiAlSiN	-462	3.61	Barshilia <i>et al.</i> 2010

It was also found that the corrosion potential, E_{corr} , of the TiAlBN nanocomposite coatings was affected by

the coating's grain size. Fig. 5 shows the correlation of E_{corr} and the grain size of the deposited TiAlBN nanocomposite coatings. It can be noted that as the grain size increases, E_{corr} decreases. This behavior can be related to the formation speed of the passive layer of TiO_2 and Al_2O_3 in the coating. According to Balyanov et al. (2004), corrosion activation occurs mainly on surface defect such as grain boundaries and dislocations. Smaller grain size will have higher fraction of grain boundaries (Qin et al. 2010). The increase of grain boundaries will provide higher fraction of nucleation sites for passive films to form, hence a faster formation of protective layer. This results in reduction of the corrosion resistance of the material. The variation in grain size is corresponding to the changes in the boron concentration of the TiAlBN nanocomposite coating as seen in the result of Rebholz et al. (2007).

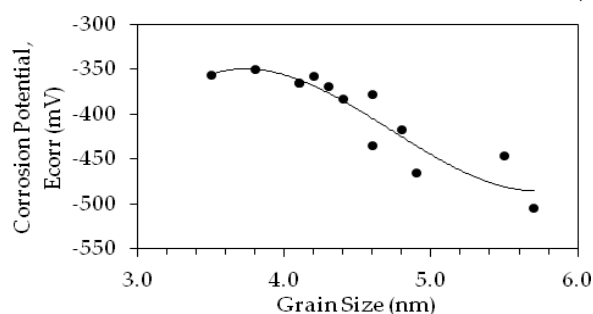


FIG. 5 CORRELATION BETWEEN CORROSION POTENTIAL, E_{corr} , WITH GRAIN SIZE OF THE TIALBN NANOCOMPOSITE COATING

In this study, it was found that the corrosion potential of the TiAlBN coated samples were lower than the uncoated sample. According to Rudenja et al. (1998), the corrosion potential can be related to the corrosion resistance of the coating. Corrosion potential indicates the initiation of material's corrosion in a potentiodynamic test. A lower corrosion potential exhibited by the TiAlBN coated samples signifies that it has a lower corrosion resistance as compared to the uncoated sample. However, the TiAlBN coated samples were still able to protect the surface of the substrate material from pitting corrosion as shown in Fig. 6, due to its extremely low corrosion rate.

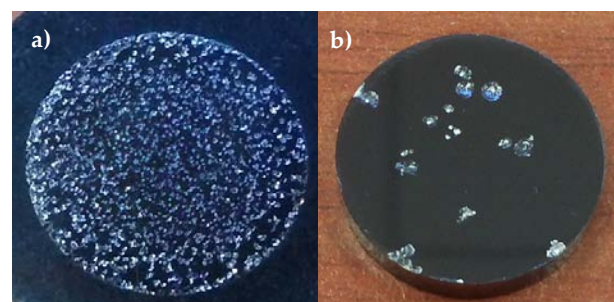


FIG. 6 PITTING CORROSION INDICATED BY WHITE SPOTS ON SAMPLE SURFACE OF, A) UNCOATED AISI 316, AND B) TIALBN COATED AISI 316

Conclusions

In this study, TiAlBN nanocomposite coating was deposited via RF magnetron sputtering using single hot-pressed Ti-Al-BN as a target. The deposited coating exhibited a range of grain size from 3.5 – 5.7 nm. Based on the findings obtained in this research, it can be concluded that the corrosion behavior of TiAlBN nanocomposite coating is affected by the grain size of the coating. A slight increase in grain size decreases the corrosion resistance of the coating. In addition, the coating was able to greatly reduce pitting corrosion of AISI 316 stainless steel, and exhibited a corrosion resistance comparable with other high corrosion resistance coatings such as (Ti,Al)N, and TiAlSiN.

ACKNOWLEDGMENT

This research was financially supported by FRGS/2010/FKP/SG03/2 F0083 grant under the 'Fundamental Research Grant Scheme' of the Ministry of Higher Education, Malaysia.

REFERENCES

- Baker M.A., Klose C., Rebholz C., Leyland A., and Matthews A. "Evaluating the Microstructure and Performance of Nanocomposite PVD TiAlBN Coatings." *Surface Coating and Technology*, vol.151-152 (2002): 338-343.
- Baker M.A., Monclus M.A., Rebholz C., Gibson P.N., Leyland A. and Matthews A. "A Study of the Nanostructure and Hardness of Electron Beam Evaporated TiAlBN Coatings." *Thin Solid Films*, vol.518 (2010): 4273-4280.
- Balyanov A., Kutnyakova J., Amirkhanova N.A., Stolyarov V.V., Valiev R.Z., Liao X.Z., Zhao Y.H., Jiang Y.B., Xu H.F., Lowe T.C. and Zhu Y.T. "Corrosion Resistance of Ultra Fine-grained Ti." *Scripta Materialia* 51, no.3 (2004): 225-229.
- Barshilia C.B., Deepthi B., and Rajam K.S. "Deposition and Characterization of TiAlN/Si₃N₄ Superhard Nanocomposite Coatings Prepared by Reactive Direct Current Unbalanced Magnetron Sputtering." *Vacuum*, vol.81 (2006): 479-488.
- Barshilia H.C., Ghosh M., Shashidhara Ramakrishna R. and Rajam K.S. "Deposition and Characterization of TiAlSiN Nanocomposite Coatings prepared by Reactive Pulsed Direct Current Unbalanced Magnetron Sputtering." *Applied Surface Science*, vol.256 (2010): 6420-6426.
- Desmaison J., Lefort P. and Billy M. "Oxidation of Mechanism of Titanium Nitride in Oxygen." *Oxidation of Metal*, Vol.13 (1979): 505-517.
- Hernandez J.M., Gonzalez L.G., Saldana J.M. and Beltran F.J.E. "Structure and Mechanical Properties of (Ti,Al)(B,N) Coatings Fabricated by Reactive DC Magnetron Sputtering." *Surface Coating and Technology*, vol.76 (2004): 161-164.
- Holmberg K. and Matthews A. *Coating Tribology: Properties, Techniques, and Application in Surface Engineering*. 2nd ed. The Netherlands: Elsevier Science B.V., 1998.
- Liu K.T. and Duh J.G. "Grain Size Effects on the Corrosion Behavior of Ni_{50.5}Ti_{49.5} and Ni_{45.6}Ti_{49.3}Al_{5.1} Films." *Journal of Electroanalytical Chemistry*, vol.618 (2008): 45-52.
- Niederberger M. and Pinna N. *Metal Oxide Nanoparticles in Organic Solvents*, London: Springer, 2009.
- Qin L.Y., Lian J.S. and Jiang Q. "Effect of Grain Size on Corrosion Behavior of Electrodeposited Bulk Nanocrystalline Ni." *Transactions of Nonferrous Metals Society of China*, vol.20 (2010): 82-89.
- Ralston K.D., and Birbilis N. "Effect of Grain Size on Corrosion: A Review." *Corrosion* 66, no.7 (2010): 075005.
- Rebholz C., Monclus M.A., Baker M.A., Mayrhofer P.H., Gibson P.N., Leyland A. and Matthews A. "Hard and Superhard TiAlBN Coatings Deposited by Twin Electron-Beam Evaporation." *Surface Coating and Technology*, vol.201 (2007): 6078-6083.
- Rebholz C., Schneider J.M., Voevidin A.A., Steinebrunner J., Charitidis C., Logothetidis S., Leyland A. and Matthews A. "Structure, Mechanical and Tribological Properties of Sputtered TiAlBN Thin Films." *Surface Coating and Technology*, vol.113 (1999): 126-133.
- Rosli Z.M., Kwan W.L., Juoi J.M., Nayan N., Mahamud Z. and Yusuf Y. "Characterization of TiAlBN nanocomposite coating deposited via radio frequency magnetron sputtering using single hot-pressed target." *Advanced Materials Research*, Vol.626 (2013): 298-301. (in press)
- Rudensja S., Leygraf C., Pan J., Kulu P., Talimets E. and Mikli V. "Duplex TiN Coatings Deposited by Arc Plating for Increased Corrosion Resistance of Stainless Steel Substrates." *Surface Coating and Technology*, vol.114 (1999): 129-136.
- Rudensja S., Kulu P., Tallimets E., Mikli V. and Straede C.A. "Corrosion Performance of Duplex TiN Coatings Deposited by Arc Plating." *Surface Coating and Technology*, vol.100-101 (1998): 247-250.
- Shtansky D.V., Kaneko K., Ikuhara Y. and Levashov E.A. "Characterization of Nanostructured Multiphase Ti-Al-B-N Thin Films with Extremely Small Grain Size." *Surface Coating and Technology*, vol.148 (2001): 206-215.
- Yoo Y.H., Le D.P., Kim J.G., Kim S.K. and Vinh P.V. "Corrosion Behavior of TiN, TiAlN, TiAlSiN Thin Films Deposited on Tool Steel in the 3.5 wt.% NaCl Solution." *Thin Solid Films*, vol.516 (2008): 3544-3548.